HAFTA-12
ANYONİK POLİMERİZASYON KİNETİĞİ

$\text{katyonik polimerizasyon}$

$\text{anyonik polimerizasyon}$

$$n\text{-}C_4H_9Li \longrightarrow n\text{-}C_4H_9^- \ Li^+$$

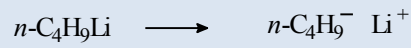$$n\text{-}C_4H_9^- \ Li^+ \ + \ H_2C = \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} \longrightarrow n\text{-}C_4H_9 - H_2C - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C^-}} \ Li^+$$

$$R' - H_2C - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C^-}} \ M^+ \ + \ H_2C = \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} \longrightarrow R' - H_2C - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - H_2C - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C^-}} \ M^+$$

$$\sim\sim - H_2C - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C^-}} \ M^+$$

sonlanma

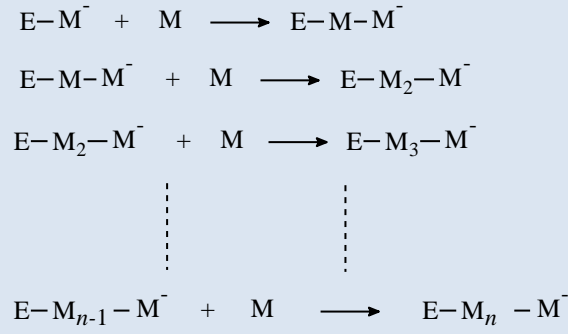$$\sim\sim - H_2C - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C^-}} \ M^+ \ + \ H^+OH^- \longrightarrow \sim\sim - H_2C - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - H \ + \ MOH$$
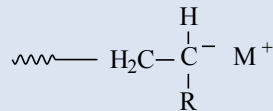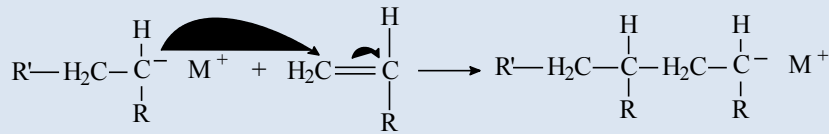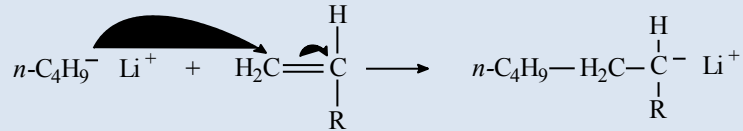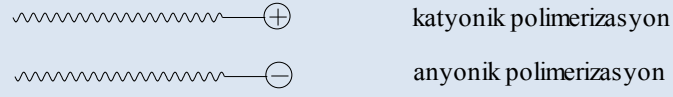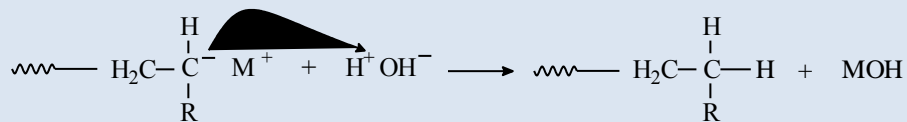
BAŞLATICININ TAMAMEN İYONLARINA AYRIŞMASI

$$EY \longrightarrow E^- \ + \ Y^+$$

$$E^- \ + \ Y^+ \ + \ M \longrightarrow E-M^- \ + \ Y^+$$

$$E-M^- \ + \ M \ \longrightarrow \ E-M-M^-$$

$$E-M-M^- \ + \ M \ \longrightarrow \ E-M_2-M^-$$

$$E-M_2-M^- \ + \ M \ \longrightarrow \ E-M_3-M^-$$

$$\vdots \qquad\qquad \vdots$$

$$E-M_{n-1}-M^- \ + \ M \ \longrightarrow \ E-M_n \ -M^-$$
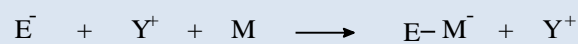
polimerizasyon hızı

$$r_p = -\frac{d[M]}{dt} = k_p^{'} [E^-][M]$$

$$r_p = -\frac{d[M]}{dt} = k_p^{'} [EY]_o \ [M]$$

$$k_p = k_p^{'} [EY]_o$$

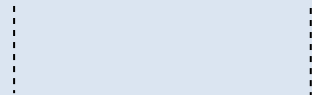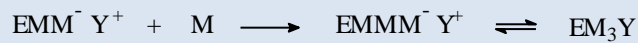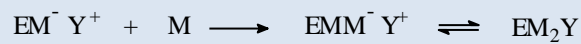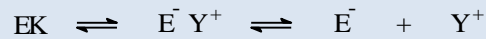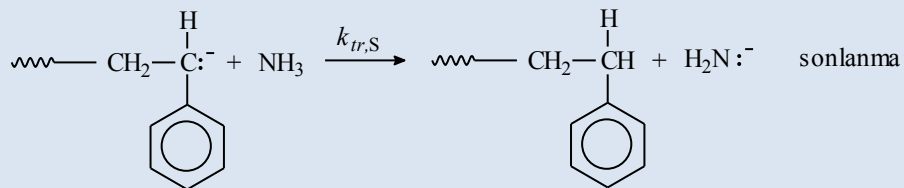$$r_p = -\frac{d[M]}{dt} = k_p [M]$$

$$\ln[M] = \ln[M]_o - k_p t$$

$$[M] = [M]_o \, e^{-k_p \, t}$$

BAŞLATICININ KISMEN İYONLARINA AYRIŞMASI

$$EK \ \rightleftharpoons \ E^- Y^+ \ \rightleftharpoons \ E^- \ + \ Y^+$$

$$E^- Y^+ \ + \ M \ \longrightarrow \ EM^- Y^+ \ \rightleftharpoons \ EMY$$

$$EM^- Y^+ \ + \ M \ \longrightarrow \ EMM^- Y^+ \ \rightleftharpoons \ EM_2Y$$

$$EMM^- Y^+ \ + \ M \ \longrightarrow \ EMMM^- Y^+ \ \rightleftharpoons \ EM_3Y$$

$$\vdots \qquad\qquad \vdots$$

$$EM_{n-1}^- Y^+ \ + \ M \ \longrightarrow \ EM_n^- Y^+ \ \rightleftharpoons \ EM_nY$$
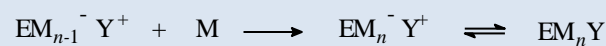
stirenin potasyum amitle anyonik polimerizasyonu

$$KNH_2 \underset{}{\overset{K}{\rightleftharpoons}} K^+ + H_2N:^-$$ 　　　　başlatıcının ayrışma dengesi

$$H_2N:^- + H_2C{=}CH \xrightarrow{k_i} H_2N{-}CH_2{-}\overset{\overset{H}{|}}{C}:^-$$ 　　başlama

$$H_2N{-}CH_2{-}\overset{\overset{H}{|}}{C}:^- + H_2C{=}CH \xrightarrow{k_p} H_2N{-}H_2C{-}CH{-}CH_2{-}\overset{\overset{H}{|}}{C}:^-$$ 　büyüme

$$\sim\!\!\sim\!\!\sim{-}CH_2{-}\overset{\overset{H}{|}}{C}:^- + NH_3 \xrightarrow{k_{tr,S}} \sim\!\!\sim\!\!\sim{-}CH_2{-}\overset{\overset{H}{|}}{CH} + H_2N:^-$$ 　sonlanma

$$EY = KNH_2$$

$$E^- = H_2N:^-$$

$$Y^+ = K^+$$

$$EM^- = H_2N{-}CH_2{-}\overset{\overset{H}{|}}{C}:^-$$
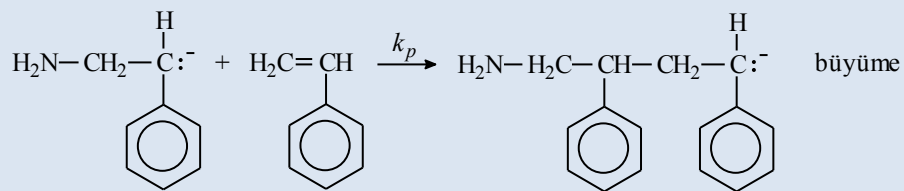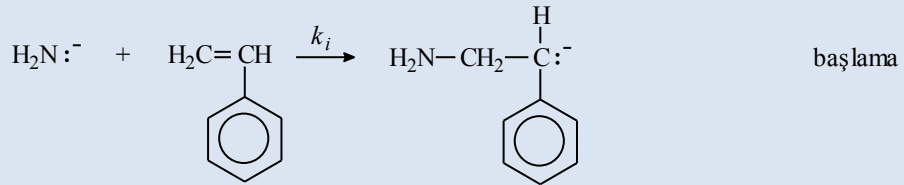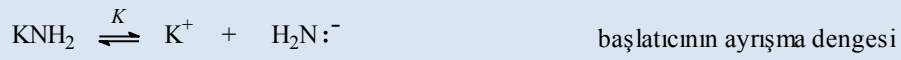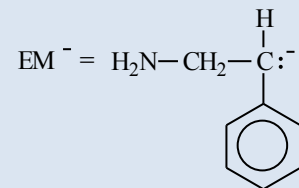
$$r_i = k_i\left[NH_2^-\right][M]$$

$$r_p = k_p\left[M^-\right][M]$$

$$r_t = k_{tr,S}\left[M^-\right][NH_3]$$

$$\left[NH_2^-\right] = K\frac{\left[KNH_2\right]}{\left[K^+\right]}$$

$$r_i = k_i \, K \, \frac{[KNH_2][M]}{[K^+]}$$

$$[M^-] = \frac{k_i}{k_{tr,S}} K \, \frac{[KNH_2][M]}{[K^+][NH_3]}$$

$$r_p = k_p \, \frac{k_i}{k_{tr,S}} K \, \frac{[KNH_2][M]^2}{[K^+][NH_3]}$$

$$K = \frac{[NH_2^-][K^+]}{[KNH_2]}$$

$$[K^+] = K^{1/2} [KNH_2]^{1/2}$$

$$r_p = k_p \, \frac{k_i}{k_{tr,S}} K^{1/2} \, \frac{[KNH_2]^{1/2} [M]^2}{[NH_3]}$$

$$r_i = k_i \, K^{1/2} [KNH_2]^{1/2} [M]$$